



⑪ Publication number : **0 409 782 B1**

⑫

## EUROPEAN PATENT SPECIFICATION

④⑤ Date of publication of patent specification :  
**15.06.94 Bulletin 94/24**

⑤① Int. Cl.<sup>5</sup> : **C08L 3/02, C08L 51/02**

②① Application number : **90810534.9**

②② Date of filing : **12.07.90**

⑤④ **Polymer base blend compositions containing destructured starch.**

③⑥ Priority : **18.07.89 US 381620**  
**08.12.89 US 447747**

④③ Date of publication of application :  
**23.01.91 Bulletin 91/04**

④⑤ Publication of the grant of the patent :  
**15.06.94 Bulletin 94/24**

⑧④ Designated Contracting States :  
**AT BE CH DE DK ES FR GB GR IT LI LU NL SE**

⑤⑥ References cited :  
**EP-A- 0 327 505**  
**GB-A- 2 009 762**  
**GB-A- 2 190 093**  
**US-A- 3 485 777**

⑦③ Proprietor : **WARNER-LAMBERT COMPANY**  
**201 Tabor Road**  
**Morris Plains New Jersey 07950 (US)**

⑦② Inventor : **Lentz, David John, Dr.**  
**23 Timber Lane**  
**Randolph, N.J. 07869 (US)**  
Inventor : **Sachetto, Jean-Pierre, Dr.**  
**Düchelweiher 13**  
**CH-4144 Arlesheim (CH)**  
Inventor : **Silbiger, Jakob, Dr.**  
**Oberwilerstrasse 72**  
**CH-4054 Basel (CH)**

⑦④ Representative : **Silbiger, Jakob**  
**c/o André Braun**  
**European Patent Attorney**  
**Murtengasse 5**  
**CH-4051 Basel (CH)**

**EP 0 409 782 B1**

Note : Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

## Description

The present invention relates to polymer compositions capable of being formed by heat and pressure into articles having dimensional stability and enhanced physical properties, and to pre-mixes useful for preparing these compositions. These compositions and pre-mixes comprise destructurez starch and other polymers as described herein.

It is known that natural starch which is found in vegetable products and which contains a defined amount of water can be treated at an elevated temperature and in a closed volume, thereby at elevated pressures, to form a melt. The process is conveniently carried out in an injection molding machine or extruder. The starch is fed through the hopper onto a rotating, reciprocating screw. The feed material moves along the screw towards the tip. During this process, its temperature is increased by means of external heaters around the outside of the barrel and by the shearing action of the screw. Starting in the feed zone and continuing in the compression zone, the particulate feed becomes gradually molten. It is then conveyed through the metering zone, where homogenization of the melt occurs, to the end of the screw. The molten material at the tip can then be treated further by injection molding or extrusion or any other known technique to treat thermoplastic melts, to obtain shaped articles.

This treatment, which is described in the European Patent Application No. 84 300 940.8 (Publication No. 118 240), which patent is incorporated herein by reference, yields an substantially destructurez starch. As described in the above mentioned patent, the reason for this is that the starch is heated above the glass transition and the melting temperatures of its components. As a consequence, a melting and disordering of the molecular structure of the starch granules takes place, so that an substantially destructurez starch is obtained. The expression "destructurez starch" defines starch obtained by such thermoplastic melt formation. Reference is also made to European Patent Applications No. 88810455.1 (Publication No. 298,920), No. 88810548.3 (Publication No. 304,401) and No. 89810046.6 (Publication No. 326,517), which further describe destructurez starch, methods for making it, and uses of it. These applications are also incorporated herein by reference.

It is preferred that the destructurez starch used in the present invention has been heated to a high enough temperature and for a time long enough so that the specific endothermic transition analysis as represented by a differential scanning calometry (DSC) curve indicates that a specific relatively narrow peak just prior to oxidative and thermal degradation has disappeared, as described in the above-mentioned European Patent Application No. 89810046.6 (Publication No. 326,517).

Destructurez starch is a new and useful material for many applications. An important property is its biodegradability. In humid air, however, destructurez starch takes up water from the air, thereby increasing its moisture content. As a consequence, a shaped article made from destructurez starch may under such conditions lose its dimensional stability. On the other hand such an article may dry out in low humidity and become brittle.

Thermoplastic starch has essentially a unique set of properties and while these are very useful, they may limit its utility in cases where a softer, more resilient or harder, tougher polymer is desired.

Thermoplastic starch as mentioned can be extruded and molded into numerous useful shapes and profiles. However, the processing parameters such as water content, temperature, and pressure are critical and must be narrowly controlled to achieve reproducible quality products. This is a further disadvantage for many applications.

To overcome these potential limitations, it would be useful to increase the dimensional stability over a wide humidity range; to increase the toughness (measured as break energy); to increase the elasticity (measured as elongation); to decrease polymer stiffness (measured as Young's modulus) and increase the hardness.

Broadening processing latitude increases the variety of shapes and composites and decreases the need for close controls. It would therefore also be useful to improve the control of the melt strength, e.g. increasing the processing latitude for extruding, injection molding, film blowing or fiber drawing and to control the surface tack and adhesion to other substrates.

Conventional thermoplastic materials are hydrophobic, substantially water-insoluble polymers which are conventionally processed in the absence of water and volatile materials. Starch to the contrary forms a melt in the presence of water but decomposes at elevated temperature, i.e. around 240°C. It was therefore expected that such a starch melt could not be used as a thermoplastic component together with hydrophobic, substantially water-insoluble polymeric materials not only because starch forms a melt in the presence of water as described above, but also because of its chemical structure and hydrophilic nature.

EP-A-0 118 240 as mentioned above, discloses destructurez starch and method of its production. GB-A-2 009 762 refers to compounds related to the component b) of the present invention for the use as containers in growing seedlings. US-A-3 485 777 refers to the compatibilization of normally incompatible polymers which

do not contain starch. GB-A-2 190 093 refers to moldable starch compositions comprising destructurized starch, specifically to particulate, free-flowing starch based compositions. Polyvinylalcohols and cellulose derivatives may be optional additives. The addition of a compound as defined as component b) of the present invention is not mentioned there. EP-A-0 327 505 was filed prior to the filing date of the present invention but published on August 9, 1998. This document discloses compositions comprising destructurized starch and at least one essentially water-insoluble synthetic polymer. Compounds as defined herein as component b) are not mentioned in EP-A-0 327 505. None of these documents teaches compositions comprising the three components a), b) and c) as taught in the present invention.

It has now been found that starch, when heated in a closed volume at proper moisture and temperature conditions as described above to form a melt of destructurized starch, is substantially compatible in its processing with melts formed by hydrophobic substantially water insoluble thermoplastic polymers and that the two types of molten materials show an interesting combination of properties, especially after the melt has solidified.

One very important aspect is the surprisingly improved dimensional stability of such destructurized starch blended with such hydrophobic thermoplastic materials. Such polymer compositions are described in copending European Patent Application No. 89810078.9 (Publication No. 327,505), which is incorporated herein by reference. Although articles made from such compositions possess better dimensional stability than those made from destructurized starch alone, the physical properties of the therein-described compositions are not as good as might be desired for some end uses. In particular, it is important that articles made from destructurized starch compositions retain sufficient strength and dimensional stability to perform their desired function while still being biodegradable after disposal.

It has now been found that articles made from such destructurized starch blended with specific hydrophobic thermoplastic materials as described herein show a surprising increase in all or a part of their physical properties and behaviour of their melts as to overcome the limitations as explained above. Moreover it was surprisingly found that many of the blends described herein show a significantly improved dimensional stability in humid air compared with non-blended destructurized starch whilst retaining a surprisingly high degree of disintegration in contact with liquid water which in consequence leads to a high degree of biodegradability.

In order to achieve such properties, it has been found useful to make polymer compositions comprising: a) destructurized starch, b) at least one compound selected from the group consisting of polysaccharide graft copolymers and graft copolymers of polysaccharide derivatives (referred to herein as "component b)"), and optionally c) a substantially water-insoluble polymer different from those defined as component b). In one aspect, the present invention relates to a composition comprising destructurized starch and component b). This composition is useful itself for making finished articles, but it is primarily useful as a "pre-mix" for combining with the substantially water-insoluble polymer. In a second aspect, the invention comprises the ternary composition of destructurized starch, component b), and at least one substantially water-insoluble polymer (component c)). These compositions may be in the form of powdery mixtures of the components, melts, or solid forms. The invention also includes methods for making and using both above - described compositions and shaped articles made therefrom.

Specifically the present invention refers to a composition consisting of

- a) destructurized starch produced by heating a starch having a water content of 5 to 40% by weight based on the starch/water component, in a closed volume under shear; and at a temperature of 130°C to 190°C above the glass transition and the melting points of its components and at a pressure of up to  $150 \times 10^5$  N/m<sup>2</sup> to form a melt whereby the pressure corresponds at a minimum to the vapour pressure of water at the temperature used and heating the melt for a time long enough to obtain a melting of the molecular structure of the starch granules and a homogenization of the melt;
- b) at least one compound as defined in Table 1;

Table 1

No.	Polysaccharide	grafted monomer	weight% graft	n	M <sub>w</sub> (x10 <sup>3</sup> )
1	starch	styrene	40	6.8	710
2	"	isoprene	25	5.8	400
3	"	acrylonitrile	49	9.2	500
4	"	methyl methacrylate	50	13.6	1,360
5	"	methyl acrylate	42	9.8	845
6	"	methyl acrylate/ butyl/acrylate	50	6.25	700
7	"	acrylic acid	45	9.2	450
8	"	acrylamide	52	9.2	500
9	"	beta-propio- lactone	40	1.4	100

Table 1 (cont.)

No.	Polysaccharide	grafted monomer	weight% graft	n	M <sub>w</sub>
10	"	ethylenimine	42	1.7	75
11	"	propylenimine	35	1.2	70
12	"	caprolactam	30	0.4	50
13	"	alkylammonium			
14	"	acrylate	40	2.6	600
15	"	methyl vinyl ether	40	10.3	600
16	amylose	acrylamide/Na acrylate	60	9.2	500
17	"	butyl acrylate	50	4.7	600
18	"	butyl acrylate/			
19	"	acrylonitrile	40	3.0	550
20	"	ethyl acrylate	45	6.5	650
21	"	ethyl acrylate/			
22	dextrin	acrylonitrile	45	8.1	625
23	"	acrylamide	48	9.0	490
24	"	acrylonitrile	47	8.3	450
25	carboxyl cellulose	styrene	50	6.25	650
26	"	butadiene	40	4.6	250
27	"	butadiene/			
28	alginate	styrene	42	4.0	320
29	"	acrylamide	45	2.8	200
30	"	acrylonitrile	42	8.3	450
31	"	styrene	48	5.0	520
32	"	butadiene	40	5.7	310
33	"	methyl methacrylate	43	3.4	340
34	cellulose	styrene	27.8	5.4	560
35	"	acrylonitrile	27.0	7.7	420
36	"	styrene/			
37	"	acrylonitrile	26.0	5.7	450
38	"	acrylamide	17.0	4.4	320
39	"	acrylic acid	15.0	4.2	300

Table 1 (cont.)

No.	Polysaccharide	grafted monomer	weight% graft	n	M <sub>w</sub>
35	cellulose	methyl-methacrylate	28.9	2.5	250
36	"	methyl acrylate	36.0	3.2	280
37	"	ethyl acrylate	34.0	3.1	310
38	"	butyl acrylate	29.4	2.3	300
39	"	isobutyl acrylate	29.6	1.7	220
40	"	butadiene	25.0	3.5	190
41	"	butadiene/styrene	24.0	2.6	210
42	"	isoprene	20.0	2.6	180
43	"	methacrylamide	25.0	2.2	190
44	"	vinyl acetate	22.0	2.7	230
45	"	vinyl chloride	20.0	3.12	195
46	"	ethylene	16.0	3.6	100
47	ethyl cellulose	methacrylic acid	35	3.8	325
48	"	methyl-methacrylate	32	3.0	300
49	"	styrene	29	2.4	250
50	"	vinyl acetate	30.5	2.3	200
51	hydroxyethyl-cellulose	butyl acrylate	35	2.2	280
52	"	butyl acrylate/acrylonitrile	40	2.2	200
53	"	ethyl acrylate	41	1.9	190
54	"	ethyl acrylate/acrylonitrile	45	2.7	210
55	methyl cellulose	acrylonitrile	40	4.6	250
56	cellulose acetate	acrylamide	20	2.8	200
57	"	acrylonitrile	25	3.5	190
58	"	methyl acrylate	22	2.6	220
59	"	ethyl acrylate	24	2.3	230
60	"	methyl methacrylate	20	2.2	220
61	"	vinyl acetate	20	2.3	200

n = average number of grafted monomeric units

M<sub>w</sub> = average molecular weight of grafted polymers

c) a thermoplastic polymer which undergoes melt formation at a set processing temperature within the range of 95°C to 190°C and is selected from (i) the group consisting of polyolefines, polyacrylonitriles, polyacrylates, polymethacrylates, polyacetals, polyamides, thermoplastic polyesters, thermoplastic polyurethanes, polycarbonates, polyarylethers, (ii) alkylene/-vinyl ester-copolymers, ethylene vinyl acetate

copolymers, ethylene/vinyl alcohol copolymers, ethylene/ethyl acrylate copolymers, ethylene/methacrylate copolymers, styrene/acrylonitrile copolymers, ethylene/maleic anhydride copolymers and mixtures thereof;

5 d) optionally one or more materials selected from the group consisting of fillers, lubricants, mold release agents, plasticizers, foaming agents, stabilizers, flow accelerators, coloring agents, pigments and mixtures thereof;

wherein the ratio of the destructured starch to component b) varies from 99:1 to 80:20 and wherein the sum of the components b) and c) constitutes at least 50% and up to 80% by weight of the total composition.

10 The present invention includes said polymer compositions in the form of powdery mixtures of their components, in the form of melts, or in solidified form.

Component b) is chosen as described herein to be substantially compatible with the starch and also to promote the compatibility of component c) with the combination of starch and component b).

15 The present invention further refers to a method of producing said polymer compositions in the molten or solid form as well as a method of producing shaped articles from said polymer compositions, and to the resulting shaped articles made therefrom.

The polymer compositions of the present invention are prepared by admixing destructured starch, component b) and optionally component c) and any further additives. This mixture is then heated in a closed volume to elevated temperatures until a homogeneous melt is obtained, and shaped articles can be formed therefrom.

20 An alternate method of producing the polymer compositions of the present invention comprises: Heating starch which is in a condition to be destructured, in a closed volume to elevated temperatures and at elevated pressures for a time sufficient to destructure the starch and form a melt; adding component b) as well as other polymer or polymers and/or additives before, during or after such starch destructure; and continuing to heat the mixture until a homogeneous melt is obtained. It is preferred that component b) and, if desired, component c), as well as other additives be combined with the starch and the combination formed into a melt. The starch in this combination may be already wholly or partially destructured or the destructure may take place during melt formation.

30 The present invention further refers to the process of working said polymer composition under controlled water content, temperatures and pressure conditions as a thermoplastic melt wherein said working process is any known process, such as, for example injection molding, blow molding, extrusion, coextrusion, compression molding, vacuum forming, thermoforming or foaming. All of these processes are collectively referred to herein as "forming".

35 The term "starch" as used herein includes chemically substantially non-modified starches as for example generally carbohydrates of natural, vegetable origin, composed mainly of amylose and/or amylopectin. They can be extracted from various plants, examples being potatoes, rice, tapioca, corn (maize), pea, and cereals such as rye, oats and wheat. Preferred is starch made from potatoes, corn, wheat or rice. Mixtures of starches obtained from these sources are contemplated. It further includes physically modified starches such as gelatinized or cooked starches. It further includes pre-extruded starches, as described in the above-referenced European Patent Application No. 89810046.6 (Publication No. 326,517).

40 As described above, it has been found that starches, e.g. with a water content within the range of about 5 to about 40 % by weight based on the weight of the composition, undergo a specific narrow endothermic transition on heating to elevated temperatures and in a closed volume just prior to the endotherm change characteristic of oxidative and thermal degradation. The specific endothermic transition can be determined by differential scanning calorimetric analysis (DSC) and is indicated on the DSC-diagram by a specific relatively narrow peak just prior to the endotherm characteristic of oxidative and thermal degradation. The peak disappears as soon as the mentioned specific endothermic transition has been undergone. The term "starch" includes also treated starches wherein said specific endothermic transition has been undergone. Such starch is described in the EP 89810046.6 (Publication No. 326,517).

50 Although at the current time, destructure of starch requires the presence of water in ranges disclosed herein, the present inventive compositions also contemplate the use of destructured starch prepared by other methods, e.g. without the use of water.

55 The water content of such a starch/water composition is preferably about 5 to about 40 % water by weight of the starch/water component and preferably about 5 to about 30 %. However, in order to work with the material near its equilibrium water content to which it gets when it is finally exposed to the free atmosphere, a water content of 10 to about 22 %, preferably of 14 to about 18 % by weight calculated based on the starch/water component should be used in processing and is preferred.

The compounds of component b) are selected from the group consisting of polysaccharide graft copolymers and graft copolymers of polysaccharide derivatives.

Polysaccharides and polysaccharide graft copolymers as well as graft copolymers of polysaccharide derivatives are known and are described e.g. in Encyclopaedia of Polymer Science and Engineering, John Wiley & Sons, Volume 3, 1986. Polysaccharides are defined as natural occurring carbohydrate polymers in which monosaccharide units are linked directly through glycosidic linkages. Polysaccharides are originating from plant-, animal- and microbial kingdoms. The preferred polysaccharides are the different starches, celluloses, hemicelluloses, xylenes, gums, alginates, pectins and pullulans. The most preferred are starch and cellulose.

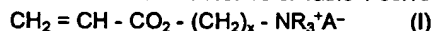
Polysaccharide derivatives are e.g. polysaccharide ethers, alkoxyated polysaccharides, such as methyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, or the analogous known derivatives from starch.

A polysaccharide graft copolymer is a polysaccharide covalently linked to a polymer so that separation by solvent extraction cannot be achieved without first degrading the polysaccharide e.g. by hydrolytic or oxidative degradation. The same is to be said analogously for graft copolymers of polysaccharide derivatives.

Graft copolymerization results from the formation of an active site at a point on the polysaccharide molecule resp. its derivative other than its end, and exposure to a polymerizable monomer.

Special compounds, their weight % graft, the average number of grafted monomeric units (n) and the average molecular weight of grafted polymers ( $M_w$ ) are given in Table 1 above.

The alkylammonium acrylates mentioned under No. 13 of Table 1 correspond to the formula



wherein

x = 2, 3 or 4, preferably 2 or 3,

R = methyl or ethyl, preferably methyl

A = an anion, preferably chloride or acetate, preferably acetate.

Preferred from Table 1 are the compounds Nos. 1, 3, 5, 7, 9, 10, 11, 12, 13, 14, 17, 20, 21, 22, 25, 26, 29, 30, 31, 33, 34, 36, 43, 44, 45, 46, 49, 50, 55, 57, 61.

Most preferred from Table 1 are the compounds Nos. 1, 3, 4, 5, 6, 9, 10, 12, 14, 16, 21, 22, 25, 30, 44, 46, 61.

As mentioned above, the polymer composition comprising the components a) and b) optionally contains one or more substantially water-insoluble hydrophobic polymers (component c), as well as further additives.

The component c) is an substantially water-insoluble polymer or a mixture of such substantially water-insoluble polymers. Component c) is preferably present in an amount effective to enhance the physical properties of articles made from the composition of the invention (which amount is sometimes referred to herein as an "effective amount" of component c)), for example increase of dimensional stability of final products made therefrom or adjust the degree of biodegradability.

As used herein a "substantially water-insoluble thermoplastic polymer" is a polymer which preferably absorbs less than 10 %, preferably less than 5 % water per 100 grams of the polymer at room temperature and preferably at a rate of less than 2 % per 100 grams of the polymer at room temperature.

Examples of substantially water-insoluble thermoplastic materials are polyolefines, such as polyethylene (PE), polyisobutylenes, polypropylenes; polyacrylonitriles (PAN); essentially water-insoluble polyacrylates or polymethacrylates; polyacetals; polyamides (PA), polyesters, polyurethanes, polycarbonates, poly(alkylene terephthalates); polyarylethers

Further included are substantially water-insoluble thermoplastic copolymers known such as alkylene/vinyl ester-copolymers preferably ethylene/vinyl acetate-copolymers (EVA); ethylene/vinyl alcohol-copolymers (EVAL); alkylene/acrylates or methacrylate copolymers preferably ethylene/acrylic acid copolymers (EAA); ethylene/ethyl acrylate-copolymers (EEA); ethylene/methyl acrylate-copolymers (EMA); ABS-copolymers; styrene/acrylonitrile-copolymers (SAN); as well as mixtures thereof.

Preferred from these are those which undergo melt formation at a set processing temperature within the range of 95°C to about 190°C.

Also preferred are those polymers containing polar groups such as ether, amide, or urethane groups. Such polymers include e.g. copolymers of ethylene, propylene or isobutylene with vinyl compounds such as, ethylene/vinyl alcohol-copolymers (EVAL), styrene/acrylonitrile-copolymers (SAN); block copolymers of amide-ethers, amide-esters; block copolymers of urethane-ethers, urethane-esters; as well as their mixtures.

Such substantially water-insoluble thermoplastic polymers may be added in any desired amount as described herein.

Such polymers may be used in any known form. Their molecular weight is also generally known in the art. It is also possible to use such polymers of relatively low molecular weight (oligomers). The choice of a particular molecular weight range is a matter of optimization and routine experimentation known to the one skilled in the art.

In the composition according to this invention, the two components a) and b) or the three components



a), b) and c) always add up to 100 % and the values of the components given in percent hereinbelow refer to the sum of 100 %.

The ratio of destructurez starch to component b) may vary preferably from about 99 : 1 to 80 : 20.

The ratio of destructurez starch to the sum of components b) and c) can be 1 : 99 to 99 : 1. It is however preferred that the destructurez starch contributes noticeably to the properties of the final material. Therefore, it is preferred that the destructurez starch is present in an amount of at least about 20 %, more preferably about 50 % and most preferably in the range of about 60 % to about 95 % by weight of the entire composition. That is, the sum of the components b) and c) are present in amounts of about 80 % or less, more preferably less than or equal to about 50 % and most preferably in the range of about 40 % to about 5 % by weight of the entire composition.

Component b) is a relatively polar material. When it functions in the present compositions in combination with component c), it is able to mix more readily with a more polar component c) than with a less polar one. Accordingly, with more polar components c), relatively less of component b) will be required than with less polar ones. The skilled worker will be able to select appropriate ratios of components b) and c) to obtain a substantially homogenous melt composition.

If the destructurez starch contains water, the percentage of this destructurez starch component is meant to be the destructurez starch/water component, i.e. including the weight of water.

The starch may be mixed prior to destructurez with additives as named hereinbelow to yield a free flowing powder useful for continuous processing and is destructurez and granulated before it is mixed with components b) and c) or the other optionally added components. The other components to be added are preferably granulated to a granular size equal to that of the granulated destructurez starch.

However, it is possible to process native starch or pre-extruded and/or destructurez granulated or powdered starch together with powdered or granulated additives and/or the polymeric material in any desired mixture or sequence.

Thus, it is preferred that components a), b) and c) as well as other conventional additives be mixed in a standard mixer. This mixture can then be passed through an extruder to produce granulates or pellets as one form of shaped articles which are also useful as starting material for processing into other articles. However, it is possible to avoid granulating and to process the obtained melt directly using down-stream equipment to produce films, blown films included, sheets, profiles, pipes, tubes, foams or other shaped articles. The sheets can be used for thermoforming.

It is preferred that fillers, lubricants and/or plasticizers be added to the starch before destructurez. However, the addition of the coloring agents as well as of components b), c) and additives other than the aforementioned can be added before, during or after destructurez.

The substantially destructurez starch/water component or granules have a preferred water content in the range of 10 to 22 % by weight of the starch/water component, more preferably 12 to 19 % and most preferably 14 to 18 % by weight of the starch/water component.

The water content described above refers to the percentage of water relative to the weight of the starch/water component within the total composition and not to the weight of the total composition itself, which would include also the weight of any added substantially water-insoluble thermoplastic polymer.

In order to destructurez the starch and/or to form a melt of the new polymeric composition according to this invention, it is suitably heated in a screw and barrel of an extruder for a time long enough to effectuate destructurez and melt formation. The temperature is preferably within the range of 130°C to 190°C depending on the type of starch used. For this destructurez and melt formation, the composition is heated in a closed volume. A closed volume can be a closed vessel or the volume created by the sealing action of the unmolten feed material as happens in the screw and barrel of injection molding or extrusion equipment. In this sense the screw and barrel of an injection molding machine or an extruder is to be understood as being a closed vessel. Pressures created in a closed vessel correspond to the vapour pressure of water at the used temperature but of course additional pressure may be applied and/or generated as normally occurs in a screw and barrel. The preferred applied and/or generated pressures are in the range of pressures which occur in extrusion and are known per se, e.g. from 5 to 150 x 10<sup>5</sup> N/m<sup>2</sup> preferably from 5 to 75 x 10<sup>5</sup> N/m<sup>2</sup> and most particularly from 5 to 50 x 10<sup>5</sup> N/m<sup>2</sup>. If the thus-obtained composition is comprised only of destructurez starch, it may be granulated and ready to be mixed with the further components according to a chosen mixing and processing procedure to obtain the granular mixture of the destructurez starch/polymer starting material to be fed to the screw barrel.

However, the obtained melt in the screw and barrel may be injection molded directly into a suitable mold, i.e. directly further processed to a final product if all necessary components are already present.

Within the screw, the granular mixture obtained as described above is heated to a temperature which is generally within the range of 130°C to 190°C. Preferably, such mixture is heated to a sufficiently high temper-

ature and for a time long enough until the endothermic transition analysis (DSC) indicates that the specific relatively narrow peak just prior to the endotherm characteristic of oxidative and thermal degradation of starch has disappeared.

5 The minimum pressures under which the melts are formed correspond to the water vapour pressures produced at said temperatures. The process is carried out in a closed volume as explained above, i.e. in the range of the pressures which occur in extrusion or molding processes and known per se, e.g. from zero to  $150 \times 10^5$  N/m<sup>2</sup> preferably from zero to  $75 \times 10^5$  N/m<sup>2</sup> and most particularly from zero to  $50 \times 10^5$  N/m<sup>2</sup>.

When forming a shaped article by extrusion the pressures are preferably as mentioned above. If the melt according to this invention is, e.g., injection molded, the normal range of injection pressures used in injection molding is applied, e.g. from  $300 \times 10^5$  N/m<sup>2</sup> to  $3000 \times 10^5$  N/m<sup>2</sup> and preferably from  $700 \times 10^5$  to  $2200 \times 10^5$  N/m<sup>2</sup>.

Accordingly the present invention provides a thermoplastic destructurized starch product formed by the process comprising:

1) providing a mixture consisting of:

- 15 - a starch composed mainly of amylose and /or amylopectin and having a water content of from 5% to 40% by weight;
- at least one polymer as defined herein above as component b);
- a thermoplastic polymer as defined herein above as component c);

wherein the ratio of the destructurized starch to component b) varies from 99:1 to 80:20 and wherein the sum of the components b) and c) constitutes at least 50% and up to 80% by weight of the total composition;

20 2) heating said mixture in the screw and barrel of an injection molding machine or an extruder at a temperature of 130°C to 190°C and at a pressure of up to  $150 \times 10^5$  N/m<sup>2</sup> to form a melt and heating the melt for a time long enough to obtain a destructurization of the starch and a homogenization of the melt;

3) shaping the melt into an article; and

25 4) allowing the shaped article to cool to a solidified dimensionally stable article.

Various hydrophilic polymers may be used as additives. These include water-soluble and water-swella-  
ble polymers.

As such it includes animal gelatin; vegetable gelatins; proteins such as sunflower protein, soybean proteins, cotton seed proteins, peanut proteins, rape seed proteins, acrylated proteins; water-soluble polysaccharides, alkyl celluloses, hydroxyalkyl celluloses and hydroxyalkylalkyl celluloses, such as methyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxyethylmethyl cellulose, hydroxypropylmethyl cellulose, hydroxybutylmethyl cellulose, cellulose esters and hydroxyalkyl cellulose esters such as cellulose acetylphthalate (CAP), hydroxypropylmethyl cellulose (HPMCP); analogous known polymers made from starch; water-soluble or water-swella-  
ble synthetic polymers such as: polyacrylates, polymethacrylates, polyvinyl alcohols, shellac and other similar polymers.

Preferred are synthetic polymers, most preferably polyacrylates, polymethacrylates, polyvinyl alcohols.

Such hydrophilic polymers may optionally be added up to 50 % based on the starch/water component, preferably up to 30 % and most preferably between 5 % and 20 % based on the starch/water component. If any hydrophilic polymer is added, its mass should be considered along with the starch in determining the appropriate amount of water in the composition.

40 Other useful additives may be e.g. adjuvants, fillers, lubricants, mold release agents, plasticizers, foaming agents, stabilizers, coloring agents, pigments, extenders, chemical modifiers, flow accelerators, and mixtures thereof.

Examples for fillers are inorganic fillers, such as the oxides of magnesium, aluminum, silicon, titanium, etc. preferably in a concentration in the range of 0.02 to 50 % by weight preferably 0.20 to 20 % based on the total weight of all the components.

Examples for lubricants are stearates of aluminum, calcium, magnesium and tin as well as talc, silicones, etc. which may be present in concentrations of 0.1 to 5 % preferably at 0.1 to 3 % based upon the weight of the total composition.

50 Examples of plasticizers include low molecular poly(alkylene oxides), such as poly(ethylene glycols), poly(propylene glycols), poly(ethylene-propylene glycols); organic plasticizers of low molar masses, such as glycerol, pentaerythritol, glycerol monoacetate, diacetate or triacetate; propylene glycol, sorbitol, sodium diethylsulfosuccinate, added in concentrations ranging from 0.5 to 15 %, preferably ranging from about 0.5 to about 5 % based on the total weight of all the components. Examples of colouring agents include known azo  
55 dyes, organic or inorganic pigments, or colouring agents of natural origin. Inorganic pigments are preferred, such as the oxides of iron or titanium, these oxides, known per se, being added in concentrations ranging from 0.001 to 10 %, preferably 0.5 to 3 %, based on the weight of all the components.

There may further be added compounds to improve the flow properties of the starch material such as an-

imal or vegetable fats, preferably in their hydrogenated form, especially those which are solid at room temperature. These fats have preferably a melting point of 50°C or higher. Preferred are triglycerides of C<sub>12</sub> -, C<sub>14</sub> -, C<sub>16</sub> -, and C<sub>18</sub> - fatty acids.

These fats can be added alone without adding extenders or plasticizers.

5 These fats can advantageously be added alone or together with mono- and/or diglycerides or phosphatides, especially lecithin. The mono- and diglycerides are preferably derived from the types of fats described above, i.e. from C<sub>12</sub> -, C<sub>14</sub> -, C<sub>16</sub> -, and C<sub>18</sub> - fatty acids.

The total amount of fats, mono-, diglycerides and/or lecithins used are up to 5 % and preferably within the range of 0.5 to 2 % by weight of the total weight of starch and any added hydrophilic polymer.

10 The materials may further contain stabilizers, such as antioxidants, e.g. thiobisphenols, alkylidenbisphenols secondary aromatic amines; light stabilizers such as UV-absorbers and UV-quenchers; hydroperoxide decomposer; free-radical scavengers; stabilizers against microorganisms.

The compositions of the invention form thermoplastic melts on heating and in a closed volume, i.e. under conditions of controlled water-content and pressure. Such melts can be processed just like conventional thermoplastic materials, using, for example, conventional apparatus for injection molding, blow molding, extrusion and coextrusion (rod, pipe and film extrusion), compression molding, foaming, to produce known articles. The articles include bottles, sheets, films, packaging materials, pipes, rods, laminated films, sacks, bags, pharmaceutical capsules, granules, powders or foams.

For example, these compositions may be used to prepare low density packaging materials (e.g. foams) by well-known methods. Conventional blowing agents may be utilized if desired or, for certain compositions, the water itself may act as the blowing agent. Open cell and closed cell foams may be produced as desired by varying the composition and processing conditions. These foams produced from the present compositions will demonstrate improved properties (e.g., dimensional stability, moisture resistance) when compared with foams made of starch without incorporation of the components b) and c) according to this invention.

25 These compositions may be used as carrier materials for active substances, and may be mixed with active ingredients such as pharmaceuticals and/or agriculturally active compounds such as insecticides or pesticides for subsequent release applications of these ingredients. The resulting extruded materials can be granulated or worked to fine powders.

The following examples are provided to further explain and exemplify the invention but not to limit the scope thereof, which scope is defined by the appended claims.

#### Example 1

35 (a) 5000 g of potato starch containing 14.5 % water are placed in a high speed mixer and 500 g of water are added under stirring. To the above mixture of starch and water, 42 g of starch-g-polystyrene containing 20 % grafted polystyrene having an average M<sub>w</sub> of 350,000 (component b)) 425 g of polystyrene polystyrol 144C (component c) sold by BASF; 42.5 g of hydrogenated fat (lubricant/release agent) sold as Boeson VP by Boehringer Ingelheim; 21.25 g of a melt flow accelerator (lecithin) sold as Metarin P by Lucas Meyer and 21.25 g of titanium dioxide (pigment and solid mixture flow accelerator) are added under stirring. The water content of the final mixture is 20.2 %.

40 (b) 5000 g of the mixture prepared under (a) are fed through a hopper into a Leistritz Single Screw Lab Extruder LSM 30 having a temperature profile of 55°C/ 145°C/ 165°C/ 165°C. The screw speed is 50 rpm. The output of extrudate is 105 g/min.

The extrudate is cut into granulates and stored for further processing.

45 (c) For further processing the granulates are conditioned to a water content of 17 % by adding water under stirring in a conventional mixer. The obtained material is then fed through a hopper to a Kloeckner-Ferromatic FM 60 injection-molding machine, for the production of tensile test pieces. The temperature profile is 90°C/ 155°C/ 155°C/ 155°C, the screw speed: 180 rpm, the shot weight 8.4 g, the residence time 450 sec., the injection pressure 1200 bar, the back pressure 30 bar.

50 All tensile test pieces are conditioned in a climatic cabinet at 50 % R.H. for five days as an arbitrary standard condition.

The test pieces are of standard DIN design (DIN No. 53455).

(d) The conditioned tensile test pieces are then tested for their stress/strain behaviour on an Instron tensile test apparatus, each test with 4 pieces.

55 The samples are measured at room temperature using an extension rate of 10 mm per minute. Results are presented in Table 1 and compared with those obtained with tensile test pieces obtained from the same starch processed in a similar way but in absence of components b) and c). It can be seen from the results that the break strain (elongation at break) is going from 15.82 % to 45 % and break energy from 194.30

$\text{kJ/m}^2$  to  $510 \text{ kJ/m}^2$  showing a considerable increase in the toughness of the blend material over the unblended one.

Table 1

	Break Strain (%)	Break Energy ( $\text{kJ/m}^2$ )
starch (unblended starch)	15.82	194.3
ternary blend Example 1	45	510

Of course different blend compositions show different values for the physical parameters indicated. To obtain the best values is a matter of optimization by varying the concentration of the different components, which is no problem to the expert in the art.

Example 1 is repeated with the following blends as per the Examples 2 to 10 whereby analogous results as given in Table 1 are obtained.

#### Example 2

Example 1 is repeated by replacing component b) by starch-g-poly(methyl acrylate) containing 42 % grafted poly(methyl acrylate) having an average  $M_w$  of 845,000, and component c) by poly(methyl methacrylate) Degalan G-6 of Degussa. The ratio of the components is varied as given in Table 2.

Table 2

Blend No.	starch: component b)+c) (weight ratio)	component b): component c) (weight ratio)
2	50 : 50	100 : 0
3	60 : 40	99 : 1
4	70 : 30	50 : 1
5	80 : 20	20 : 1
Ex. 1	91.5 : 8.5	10 : 1
6	90 : 10	1 : 1
7	94 : 6	1 : 10
8	98 : 2	1 : 50
9	99 : 1	1 : 99

The resulting injection molded polymers are tougher and more resistant to humid air than the unmodified starch polymer. The toughness as judged by resistance to breaking upon bending increases from blend 9 to blend 2 in concert with the combined increase in starch-g-poly(methyl acrylate) content. While the resistance to softening in humid atmosphere is improved in all cases relative to unblended starch, the resistance of blends 1,4,5 and 6 are particularly good. These results illustrate the unexpected combinations as benefits in performance.

Example 3

Example 1 is repeated; replacing component (b) (starch-g-polystyrene) by starch-g-poly(methyl acrylate) containing 42 % grafted poly(methyl acrylate) having an average  $M_w$  of 845,000. Component (c) (polystyrene) is replaced by the thermoplastic polyurethane elastomer Pellethane 2103-80-AEF sold by the Dow Chemical Company. The resulting injection molded polymer is tougher and more resistant to humid air than unblended starch polymer.

Example 4

Example 1 is repeated; replacing component (b) (starch-g polystyrene) by starch-g-poly(methyl methacrylate) containing 20 % of grafted poly(methyl methacrylate). The thermoplastic polyamide elastomer Pebax MA-4011 sold by Atochem is used as component (c). The resulting injection molded polymer is tougher and more resistant to humid air than unblended starch polymer.

Example 5

Example 1 is repeated; replacing component b) by starch-g-poly(methyl methacrylate) containing 20 % of grafted poly(methyl methacrylate) and replacing component c) by 212 g of the thermoplastic polyurethane elastomer Pellethane 2103-80-AEF and 212 g of the thermoplastic polyamide elastomer Pebax MA-4011. The resulting injection molded polymer is tougher and more resistant to humid air than unblended starch polymer.

**Example 6**

Example 1 is repeated; replacing component b) by starch-g-poly(methyl methacrylate) containing 20 % of grafted poly(methyl methacrylate) and replacing component c) by Nylon 12 Vestamid L-1700 sold by Huels Chemie. The resulting injection molded polymer is tougher and more resistant to humid air than unblended starch polymer.

**Example 7**

Example 1 is repeated; replacing component (b) by starch-g poly(methyl methacrylate) having 20 % grafted poly(methyl methacrylate). Component (c) is replaced by poly(methyl methacrylate) Degalan G-6 sold by Degussa. The resulting injection molded polymer is tougher and more resistant to humid air than unblended starch polymer.

**Example 8**

Example 1 is repeated; replacing component b) by starch-g-poly(methyl methacrylate) containing 20 % of grafted poly(methyl methacrylate) and replacing component c) by polyethylene Lupolen 2410T of BASF. The resulting injection molded polymer is tougher and more resistant to humid air than unblended starch polymer.

**Example 9**

Example 1 (Sections a) and b)) is repeated except that the water content is adjusted to 22 %, and the cutter is removed from the die face. A continuous extrudate is obtained which is foamed as a result of the excess water evaporation. The foam is chopped into 30-40 mm lengths and is useful as a loose-fill, packaging insulation material.

**Example 10**

During each of the injection molding operations in Examples 2 - 8 an experiment is performed to demonstrate the utility of making foams. The molten material is obtained as described in Example 1, Sections a), b) and c) in each case is extruded into the open atmosphere (Section c) instead of being injection molded into a closed mold. In every case the material is converted into a foamed extrudate useful for loose-fill in packaging applications.

**Example 11**

The granulates from Example 1 are mixed with polystyrene in the proportion of 30 to 70 parts by weight and are treated according to Example 10. The resulting foamed extrudate contains a very fine and uniform cell structure suitable for a variety of uses including structural foam.

**Claims**

1. A composition consisting of
  - a) destructurized starch produced by heating a starch having a water content of 5 to 40% by weight based on the starch/water component, in a closed volume under shear; and at a temperature of 130°C to 190°C above the glass transition and the melting points of its components and at a pressure of up to  $150 \times 10^5 \text{ N/m}^2$  to form a melt whereby the pressure corresponds at a minimum to the vapour pressure of water at the temperature used and heating the melt for a time long enough to obtain a melting of the molecular structure of the starch granules and a homogenization of the melt;
  - b) at least one compound as defined in Table 1;

Table 1

No.	Polysaccharide	grafted monomer	weight% graft	n	M <sub>w</sub> (x10 <sup>3</sup> )
1	starch	styrene	40	6.8	710
2	"	isoprene	25	5.8	400
3	"	acrylonitrile	49	9.2	500
4	"	methyl methacrylate	50	13.6	1,360
5	"	methyl acrylate	42	9.8	845
6	"	methyl acrylate/ butyl/acrylate	50	6.25	700
7	"	acrylic acid	45	9.2	450
8	"	acrylamide	52	9.2	500
9	"	beta-propio- lactone	40	1.4	100

Table 1 (cont.)

No.	Polysaccharide	grafted monomer	weight% graft	n	M <sub>w</sub>
10	"	ethylenimine	42	1.7	75
11	"	propylenimine	35	1.2	70
12	"	caprolactam	30	0.4	50
13	"	alkylammonium			
14	"	acrylate	40	2.6	600
15	"	methyl vinyl ether	40	10.3	600
16	amylose	acrylamide/Na acrylate	60	9.2	500
17	"	butyl acrylate	50	4.7	600
18	"	butyl acrylate/	40	3.0	550
19	"	acrylonitrile	45	6.5	650
20	dextrin	ethyl acrylate	45	8.1	625
21	"	ethyl acrylate/	48	9.0	490
22	carboxyl cellulose	acrylonitrile	47	8.3	450
23	"	styrene	50	6.25	650
24	"	butadiene	40	4.6	250
25	alginate	butadiene/	42	4.0	320
26	"	styrene	45	2.8	200
27	"	acrylamide	42	8.3	450
28	"	acrylonitrile	48	5.0	520
29	"	styrene	40	5.7	310
30	cellulose	butadiene	43	3.4	340
31	"	methacrylate	27.8	5.4	560
32	"	styrene	27.0	7.7	420
33	"	styrene/	26.0	5.7	450
34	"	acrylonitrile	17.0	4.4	320
	"	acrylamide	15.0	4.2	300
	"	acrylic acid			



Table 1 (cont.)

5

10	No.	Polysaccharide	grafted monomer	weight% graft	n	M <sub>w</sub>
	35	cellulose	methyl-methacrylate	28.9	2.5	250
	36	"	methyl acrylate	36.0	3.2	280
	37	"	ethyl acrylate	34.0	3.1	310
15	38	"	butyl acrylate	29.4	2.3	300
	39	"	isobutyl acrylate	29.6	1.7	220
	40	"	butadiene	25.0	3.5	190
	41	"	butadiene/styrene	24.0	2.6	210
20	42	"	isoprene	20.0	2.6	180
	43	"	methacrylamide	25.0	2.2	190
	44	"	vinyl acetate	22.0	2.7	230
	45	"	vinyl chloride	20.0	3.12	195
	46	"	ethylene	16.0	3.6	100
25	47	ethyl cellulose	methacrylic acid	35	3.8	325
	48	"	methyl-methacrylate	32	3.0	300
	49	"	styrene	29	2.4	250
	50	"	vinyl acetate	30.5	2.3	200
30	51	hydroxyethyl-cellulose	butyl acrylate	35	2.2	280
	52	"	butyl acrylate/acrylonitrile	40	2.2	200
	53	"	ethyl acrylate	41	1.9	190
35	54	"	ethyl acrylate/acrylonitrile	45	2.7	210
	55	methyl cellulose	acrylonitrile	40	4.6	250
	56	cellulose acetate	acrylamide	20	2.8	200
40	57	"	acrylonitrile	25	3.5	190
	58	"	methyl acrylate	22	2.6	220
	59	"	ethyl acrylate	24	2.3	230
	60	"	methyl methacrylate	20	2.2	220
45	61	"	vinyl acetate	20	2.3	200

n = average number of grafted monomeric units

50

M<sub>w</sub> = average molecular weight of grafted polymers

55

c) a thermoplastic polymer which undergoes melt formation at a set processing temperature within the range of 95°C to 190°C and is selected from (i) the group consisting of polyolefines, polyacrylonitriles, polyacrylates, polymethacrylates, polyacetals, polyamides, thermoplastic polyesters, thermoplastic polyurethanes, polycarbonates, polyarylethers, (ii) alkylene/vinyl ester-copolymers, ethylene vinyl

acetate copolymers, ethylene/vinyl alcohol copolymers, ethylene/ethyl acrylate copolymers, ethylene/methacrylate copolymers, styrene/acrylonitrile copolymers, and mixtures thereof;

d) optionally one or more materials selected from the group consisting of fillers, lubricants, mold release agents, plasticizers, foaming agents, stabilizers, flow accelerators, coloring agents, pigments and mixtures thereof;

wherein the ratio of the destructurized starch to component b) varies from 99:1 to 80:20 and wherein the sum of the components b) and c) constitutes at least 50% and up to 80% by weight of the total composition.

2. The composition according to claim 1 wherein component b) is selected from the compounds nos. 1, 3, 5, 7, 9, 10, 11, 12, 13, 14, 17, 20, 21, 22, 25, 26, 29, 30, 31, 33, 34, 36, 44, 45, 46, 49, 50, 55, 57, and 61 of Table 1.
3. The composition according to claim 1 wherein component b) is selected from the compounds nos. 1, 3, 4, 5, 6, 9, 10, 12, 14, 16, 21, 22, 25, 30, 44, 46, and 61 of Table 1.
4. The composition according to any one of the claims 1 to 3 wherein component b) is a graft copolymer of cellulose.
5. The composition according to any one of the claims 1 to 3 wherein component b) is a graft copolymer of starch.
6. The composition according to any one of the claims 1 to 5 wherein component c) is selected from (i) the group consisting of polyethylenes, polypropylenes, polyisobutylenes, polyamides, thermoplastic polyesters, thermoplastic polyurethanes, polycarbonates, or (ii) the group consisting of ethylene vinyl acetate copolymers, ethylene/vinyl alcohol copolymers, ethylene/ethyl acrylate copolymers, ethylene/methacrylate and mixtures thereof.
7. The composition according to any one of the claims 1 to 6 wherein the polymer of component c) absorbs water at a rate of less than 10% per 100 grams of the polymer at room temperature.
8. The composition according to any one of the claims 1 to 6 wherein the polymer of component c) absorbs water at a rate of less than 5% per 100 grams of the polymer at room temperature.
9. The composition according to any one of the claims 1 to 7 wherein the water content is from 5% to 30% by weight of the starch/water component.
10. The composition according to any one of the claims 1 to 9 wherein the water content is from 10% to 22% by weight of the starch/water component.
11. The composition according to any one of the claims 1 to 10 in the form of a melt.
12. The composition according to any one of the claims 1 to 10 in a solidified form.
13. The composition according to claim 12 in particulate, granulated or pelletized form.
14. The composition according to claim 12 in the form of a shaped article selected from the group consisting of containers, bottles, pipes, rods, packing materials, sheets, foams, films, sacks, bags and pharmaceutical capsules.
15. The composition according to claim 13 further melted and processed to form a shaped article selected from the group consisting of containers, bottles, pipes, rods, packing materials, sheets, foams, films, sacks, bags and pharmaceutical capsules.
16. The shaped articles according to claim 14 and claim 15 wherein the shaping process comprises foaming, filming, compression molding, injection molding, blow molding, extruding, co-extruding, vacuum forming, thermoforming and combinations thereof.
17. A thermoplastic destructurized starch product formed by the process comprising:
  - 1) providing a mixture consisting of:
    - a starch composed mainly of amylose and /or amylopectin and having a water content of from 5%

to 40% by weight;

- at least one polymer as defined in claim 1 as component b);
- a thermoplastic polymer as defined in claim 1 as component c);

wherein the ratio of the destructurized starch to component b) varies from 99:1 to 80:20 and wherein the sum of the components b) and c) constitutes at least 50% and up to 80% by weight of the total composition;

2) heating said mixture in the screw and barrel of an injection molding machine or an extruder at a temperature of 130°C to 190°C and at a pressure of up to  $150 \times 10^5 \text{ N/m}^2$  to form a melt and heating the melt for a time long enough to obtain a destructurization of the starch and a homogenization of the melt;

3) shaping the melt into an article; and

4) allowing the shaped article to cool to a solidified dimensionally stable article.

18. The product according to claim 17 in particulate, granulated or pelletized form.

19. The product according to claim 17 in the form of a shaped article selected from the group consisting of containers, bottles, pipes, rods, packing materials, sheets, foams, films, sacks, bags and pharmaceutical capsules.

20. The product according to claim 17 further melted and processed to form a shaped article selected from the group consisting of containers, bottles, pipes, rods, packing materials, sheets, foams, films, sacks, bags and pharmaceutical capsules.

#### Patentansprüche

1. Eine Zusammensetzung bestehend aus:

a) destrukturierter Stärke hergestellt mittels Erwärmen einer Stärke mit einem Wassergehalt von 5 bis 40 Gewichts%, bezogen auf den Stärke/ Wasser - Bestandteil, in einem geschlossenen Volumen unter Scherung; und bei einer Temperatur von 130°C bis 190°C oberhalb der Glasübergangstemp. und der Schmelzpunkte ihrer Bestandteile und bei einem Druck von bis zu  $150 \times 10^5 \text{ N/m}^2$ , um eine Schmelze zu bilden, wobei der Druck mindestens dem Wasserdampfdruck bei den verwendeten Temperaturen entspricht und unter genügend langem Erwärmen der Schmelze, um eine Schmelzung der Molekularstruktur der Stärkegranulate und eine Homogenisierung der Schmelze zu erlangen;

b) mindestens eine Verbindung, wie in Tabelle 1 definiert;

Tabelle 1

Nr.	Polysacharid	gegraftetes Monomer	Gew%-Graft	n	M <sub>w</sub>
1	Stärke	Styrol	40	6.8	710
2	"	Isopren	25	5.8	400
3	"	Acrylnitril	49	9.2	500
4	"	Methylmethacrylat	50	13.6	1,360
5	"	Methylacrylat	42	9.8	845
6	"	Methylacrylat/ Butyl/ Acrylat	50	6.25	700
7	"	Acrylsäure	45	9.2	450
8	"	Acrylamid	52	9.2	500
9	"	Beta-propiolacton	40	1.4	100
10	"	Äthylenimin	42	1.7	75
11	"	Propylenimin	35	1.2	70
12	"	Caprolactam	30	0.4	50
13	"	Alkylammonium Acrylat	40	2.6	600
14	"	Methylvinyläther	40	10.3	600
15	"	Acrylamid/ Na-acrylat	60	9.2	500

5

10

15

20

25

30

35

40

45

50

Nr.	Polysaccharid	gegraftetes Monomer	Gew%-Graft	n	M <sub>w</sub>
16	Amylose	Butylacrylat	50	4.7	600
17	"	Butylacrylat/ Acrylnitril	40	3.0	550
18	"	Äthylacrylat	45	6.5	650
19	"	Äthylacrylat/ Acrylnitril	45	8.1	625
20	Dextrin	Acrylamid	48	9.0	490
21	"	Acrylnitril	47	8.3	450
22	Carboxyl-cellulose	Styrol	50	6.25	650
23	"	Butadien	40	4.6	250
24	"	Butadien/Styrol	42	4.0	320
25	Alginat	Acrylamid	45	2.8	200
26	"	Acrylnitril	42	8.3	450
27	"	Styrol	48	5.0	520
28	"	Butadien	40	5.7	310
29	"	Methylmethacrylat	43	3.4	340
30	Cellulose	Styrol	27.8	5.4	560
31	"	Acrylnitril	27.0	7.7	420
32	"	Styrol/Acrylnitril	26.0	5.7	450
33	"	Acrylamid	17.0	4.4	320
34	"	Acrylsäure	15.0	4.2	300
35	"	Methylmethacrylat	28.9	2.5	250
36	"	Methylacrylat	36.0	3.2	280
37	"	Äthylacrylat	34.0	3.1	310
38	"	Butylacrylat	29.4	2.3	300
39	"	Isobutylacrylat	29.6	1.7	220
40	"	Butadien	25.0	3.5	190
41	"	Butadien/Styrol	24.0	2.6	210
42	"	Isopren	20.0	2.6	180
43	"	Methacrylamid	25.0	2.2	190
44	"	Vinylacetat	22.0	2.7	230
45	"	Vinylchlorid	20.0	3.12	195
46	"	Äthylen	16.0	3.6	100
47	Äthyl-cellulose	Methacrylsäure	35	3.8	325
48	"	Methylmethacrylat	32	3.0	300
49	"	Styrol	29	2.4	250
50	"	Vinylacetat	30.5	2.3	200
51	Hydroxyäthyl-cellulose	Butylacrylat	35	2.2	280
52	"	Butylacrylat/Acrylnitril	40	2.2	200
53	"	Äthylacrylat	41	1.9	190
54	"	Äthylacrylat/Acrylnitril	45	2.7	210
55	Methyl-cellulose	Acrylnitril	40	4.6	250
56	Cellulose-acetat	Acrylamid	20	2.8	200
57	"	Acrylnitril	25	3.5	190
58	"	Methylacrylat	22	2.6	220
59	"	Äthylacrylat	24	2.3	230
60	"	Methyl-Methacrylat	20	2.2	220
61	"	Vinylacetat	20	2.3	200

n = durchschnittliche Anzahl von graftedeten monomeren Einheiten  
M<sub>w</sub> = durchschnittliches Molekulargewicht der graftedeten Polymere

55

- c) ein thermoplastisches Polymer, welches eine Schmelzbildung bei einer eingestellten Verfahrenstemperatur im Bereich von 95°C bis 190°C aufweist, und ausgewählt ist von (i) der Gruppe umfassend Polyolefine, Polyacrylnitrile, Polyacrylate, Polymethacrylate, Polyacetale, Polyamide, thermoplastische Polyester, thermoplastische Polyurethane, Polycarbonate, Polyaryläther, (ii) Alkylen/ Vinylester Copolymere, Äthylen/ Vinylacetat Copolymere, Äthylen/ Vinylalkohol Copolymere, Äthylen/ Äthylacrylat Copolymere, Äthylen/ Methacrylat Copolymere, Styrol/ Acrylnitril Copolymere und deren Mischungen;
- d) gegebenenfalls ein oder mehrere Stoffe ausgewählt von der Gruppe umfassend Füllstoffe, Gleitmittel, Formtrennmittel, Plastifizierungsmittel, Schäumungsmittel, Stabilisatoren, Fließmittel, Farbstoffe, Pigmente und deren Mischungen;
- wobei das Verhältnis der destruktureierten Stärke zum Bestandteil b) zwischen 99:1 und 80:20 variiert und wobei die Summe der Bestandteile b) und c) mindestens 50 % und bis zu 80%, bezogen auf das Gewicht der gesamten Zusammensetzung, beträgt.
2. Die Zusammensetzung nach Anspruch 1, wobei Bestandteil b) ausgewählt ist von den Verbindungen Nr. 1, 3, 5, 7, 9, 10, 11, 12, 13, 14, 17, 20, 21, 22, 25, 26, 29, 30, 31, 33, 34, 36, 44, 45, 46, 49, 50, 55, 57 und 61 aus der Tabelle 1.
  3. Die Zusammensetzung nach Anspruch 1, wobei Bestandteil b) ausgewählt ist von den Verbindungen Nr. 1, 3, 4, 5, 6, 9, 10, 12, 12, 14, 16, 21, 22, 25, 30, 44, 46 und 61 aus der Tabelle 1.
  4. Die Zusammensetzung nach einem der vorhergehenden Ansprüche 1 bis 3, wobei Bestandteil b) ein Graft Copolymer aus Cellulose ist.
  5. Die Zusammensetzung nach einem der vorhergehenden Ansprüche 1 bis 3, wobei Bestandteil b) ein Graft Copolymer aus Stärke ist.
  6. Die Zusammensetzung nach einem der vorhergehenden Ansprüche 1 bis 5, wobei der Bestandteil c) ausgewählt ist von (i) der Gruppe umfassend Polyäthylen, Polypropylen, Polyisobutylen, Polyamide, thermoplastische Polyester, thermoplastische Polyurethane, Polycarbonate, oder (ii) der Gruppe umfassend Äthylen - Vinylacetat Copolymere, Äthylen/ Vinylalkohol Copolymere, Äthylen/ Äthylacrylat Copolymere, Äthylen/ Methacrylat Copolymere und deren Mischungen.
  7. Die Zusammensetzung nach einem der vorhergehenden Ansprüche 1 bis 6, wobei das Polymer des Bestandteils c) bei Zimmertemperatur Wasser in einer Menge von weniger als 10 % pro 100 Gramm Polymer absorbiert.
  8. Die Zusammensetzung nach einem der vorhergehenden Ansprüche 1 bis 6, wobei das Polymer des Bestandteils c) bei Zimmertemperatur Wasser in einer Menge von weniger als 5 % pro 100 Gramm Polymer absorbiert.
  9. Die Zusammensetzung nach einem der vorhergehenden Ansprüche 1 bis 7, wobei der Wassergehalt zwischen 5 % und 30%, bezogen auf das Gewicht des Stärke/Wasser - Bestandteils, liegt.
  10. Die Zusammensetzung nach einem der vorhergehenden Ansprüche 1 bis 9, wobei der Wassergehalt zwischen 10 % und 22%, bezogen auf das Gewicht des Stärke/Wasser - Bestandteils, liegt.
  11. Die Zusammensetzung nach einem der vorhergehenden Ansprüche 1 bis 10 in Form einer Schmelze.
  12. Die Zusammensetzung nach einem der vorhergehenden Ansprüche 1 bis 10 in fester Form.
  13. Die Zusammensetzung nach Anspruch 12 in körniger, granulierter oder tablettierter Form.
  14. Die Zusammensetzung nach Anspruch 12 in Form eines geformten Gegenstands ausgewählt von der Gruppe umfassend Behälter, Flaschen, Rohre, Stäbe, Verpackungsmaterialien, Folien, Schäume, Filme, Säcke, Beutel und pharmazeutische Kapseln.
  15. Die Zusammensetzung nach Anspruch 13 weiter geschmolzen und verarbeitet, um einen geformten Gegenstand zu bilden, ausgewählt von der Gruppe umfassend Behälter, Flaschen, Rohre, Stäbe, Verpackungsmaterialien, Folien, Schäume, Filme, Säcke, Beutel und pharmazeutische Kapseln.

16. Die geformten Gegenstände nach Anspruch 14 und Anspruch 15, wobei der Formungsvorgang Schäumen, Filmen, Pressformen, Spritzgiessen, Blasformen, Extrudieren, Coextrudieren, Vakuumformen, Thermoformen und deren Kombinationen umfasst.

- 5 17. Ein Produkt aus thermoplastischer destrukturierten Stärke geformt durch das Verfahren umfassend:
- 1) Vorlegen einer Mischung umfassend:
    - eine Stärke, hauptsächlich bestehend aus Amylose und/ oder Amylopektin und eines Wassergehalts von 5 bis 40 Gewichts-%;
    - mindestens ein Polymer, wie in Anspruch 1 als Bestandteil b) definiert;
    - 10 - ein thermoplastisches Polymer, wie in Anspruch 1 als Bestandteil c) definiert;
 wobei das Verhältnis der destrukturierten Stärke zum Bestandteil b) zwischen 99:1 und 80:20 variiert und wobei die Summe der Bestandteile b) und c) mindestens 50 % und bis zu 80 %, bezogen auf das Gesamtgewicht der Zusammensetzung, beträgt
  - 2) Erwärmen der besagten Mischung in der Schnecke und der Trommel einer Spritzgiessvorrichtung oder einer Extrudervorrichtung bei einer Temperatur von 130°C bis 190°C und bei einem Druck von bis zu  $150 \times 10^5 \text{ N/m}^2$ , um eine Schmelze zu bilden und unter genügend langem Erwärmen, um eine Destrukturierung der Stärke und eine Homogenisierung der Schmelze zu erlangen;
  - 3) Formen der Schmelze zu einem Gegenstand; und
  - 4) Abkühlen lassen des geformten Gegenstands zu einem erstarrten dimensionsstabilen Gegenstand.
- 15 18. Das Produkt nach Anspruch 17 in körniger, granulierter oder tablettierter Form.
- 20 19. Das Produkt nach Anspruch 17 in Form eines geformten Gegenstands, ausgewählt von der Gruppe umfassend Behälter, Flaschen, Rohre, Stäbe, Verpackungsmaterialien, Folien, Schäume, Filme, Säcke, Beutel und pharmazeutische Kapseln.
- 25 20. Das Produkt nach Anspruch 17 weiter geschmolzen und prozessiert, um einen geformten Gegenstand zu bilden, ausgewählt von der Gruppe umfassend Behälter, Flaschen, Rohre, Stäbe, Verpackungsmaterialien, Folien, Schäume, Filme, Säcke, Beutel und pharmazeutische Kapseln.

## Revendications

### 1. Une composition comprenant

- 35 a) de l'amidon déstructuré produit par le chauffage d'un amidon ayant une teneur en eau de 5 à 40% en poids, par rapport au constituant amidon/eau, dans un volume clos sous action de cisaillement; et à une température de 130°C à 190°C au-dessus des points de transition vitreuse et de fusion de ses constituants et à une pression allant jusqu'à  $150 \times 10^5 \text{ N/m}^2$  pour former une masse fondue, laquelle pression correspond au minimum à la pression de vapeur de l'eau à la température employée et chauffage de la masse fondue pendant un temps assez long afin d'obtenir une fusion de la structure moléculaire des granules d'amidon et une homogénéisation de la masse fondue;
- 40 b) au moins un composé comme défini dans le tableau 1;

Tableau 1

No.	polysaccharide	monomère greffé	% en poids greffé	n	M <sub>w</sub>
1	amidon	styrène	40	6.8	710
2	"	isoprène	25	5.8	400
3	"	acrylonitrile	49	9.2	500
4	"	méthyle méthacrylate	50	13.6	1,360
5	"	méthyle acrylate	42	9.8	845
6	"	méthyle acrylate/ butyle / acrylate	50	6.25	700
7	"	acide acrylique	45	9.2	450
8	"	acrylamide	52	9.2	500
9	"	beta-propio-lactone	40	1.4	100
10	"	éthylèneimine	42	1.7	75
11	"	propylèneimine	35	1.2	70
12	"	caprolactame	30	0.4	50
13	"	alkylammonium acrylate	40	2.6	600
14	"	méthyle vinyléther	40	10.3	600
15	"	acrylamide/ Na acrylate	60	9.2	500



5

No.	polysaccharide	monomère greffé	% en poids greffé	n	M <sub>n</sub>
16	amylose	butyle acrylate	50	4.7	600
17	"	butyle acrylate/acrylonitrile	40	3.0	550
18	"	éthyle acrylate	45	6.5	650
19	"	éthyle acrylate/acrylonitrile	45	8.1	625
20	dextrine	acrylamide	48	9.0	490
21	"	acrylonitrile	47	8.3	450
22	carboxyle				
23	cellulose	styrène	50	6.25	650
24	"	butadiène	40	4.6	250
25	alginate	butadiène / styrène	42	4.0	320
26	"	acrylamide	45	2.8	200
27	"	acrylonitrile	42	8.3	450
28	"	styrène	48	5.0	520
29	"	butadiène	40	5.7	310
30	cellulose	méthyle méthacrylate	43	3.4	340
31	"	styrène	27.8	5.4	560
32	"	acrylonitrile	27.0	7.7	420
33	"	styrène/ acrylonitrile	26.0	5.7	450
34	"	acrylamide	17.0	4.4	320
35	"	acide acrylique	15.0	4.2	300
36	"	méthyle méthacrylate	28.9	2.5	250
37	"	méthyle acrylate	36.0	3.2	280
38	"	éthyle acrylate	34.0	3.1	310
39	"	butyle acrylate	29.4	2.3	300
40	"	isobutyle acrylate	29.5	1.7	220
41	"	butadiène	25.0	3.5	190
42	"	butadiène/styrène	24.0	2.6	210
43	"	isoprène	20.0	2.6	180
44	"	méthacrylamide	25.0	2.2	190
45	"	acétate de vinyle	22.0	2.7	230
46	"	chlorures de vinyle	20.0	3.12	195
47	"	éthylène	16.0	3.6	100
48	éthyle de cellulose	acide méthacrylique	35	3.8	325
49	"	méthyle méthacrylate	32	3.0	300
50	"	styrène	29	2.4	250
51	"	acétate de vinyle	30.5	2.3	200
52	hydroxyéthyle de cellulose	butyle acrylate	35	2.2	280
53	"	butyle acrylate/acrylonitrile	40	2.2	200
54	"	éthyle acrylate	41	1.9	190
55	"	éthyle acrylate/acrylonitrile	45	2.7	210
56	méthyle de cellulose	acrylonitrile	40	4.6	250
57	acétate de cellulose	acrylamide	20	2.8	200
58	"	acrylonitrile	25	3.5	190
59	"	méthyle acrylate	22	2.6	220
60	"	éthyle acrylate	24	2.3	230
61	"	méthyle méthacrylate	20	2.2	220
	"	acétate de vinyle	20	2.3	200

n = nombre moyen des unités monomériques greffées

M<sub>n</sub> = poids moléculaire moyen des polymères greffés.

55

- c) un polymère thermoplastique qui subit une formation d'une masse fondue à une température de procédé réglée entre 95°C et 190°C, et choisi dans (i) le groupe comprenant polyoléfines, polyacrylonitriles, polyacrylates, polyméthacrylates, polyacétales, polyamides, polyesters thermoplastiques, polyuréthanes thermoplastiques, polycarbonates, polyaryléthers, (ii) alkylène/ ester de vinyle copolymères, éthylène/ vinylacétate copolymères, éthylène/ vinylalcool copolymères, éthylène/ éthylacrylate copolymères, éthylène/ méthacrylates copolymères, styrène/ acrylonitrile copolymères et leurs mélanges;
- d) en option une ou plusieurs matières choisies dans le groupe comprenant des charges minérales (fillers), des lubrifiants, des agents de démoulage, des plastifiants, des agents moussants, des stabilisateurs, des accélérateurs de coulée, des colorants, des pigments et leurs mélanges;
- caractérisée en ce que la proportion de l'amidon déstructuré par rapport au constituant b) varie de 99:1 à 80:20 et en ce que la somme des constituants b) et c) constitue au moins 50% et jusqu'à 80%, par rapport au poids total de la composition.
2. La composition selon la revendication 1, caractérisée en ce que le constituant b) est choisi parmi les composés N°. 1, 3, 5, 7, 9, 10, 11, 12, 13, 14, 17, 20, 21, 22, 25, 26, 29, 30, 31, 33, 34, 36, 44, 45, 46, 49, 50, 55, 57 et 61 du tableau 1.
  3. La composition selon la revendication 1, caractérisée en ce que le constituant b) est choisi parmi les composés N°. 1, 3, 4, 5, 6, 9, 10, 12, 12, 14, 16, 21, 22, 25, 30, 44, 46 et 61 du tableau 1.
  4. La composition selon l'une quelconque des revendications 1 à 3, caractérisée en ce que le constituant b) est un copolymère greffé de cellulose.
  5. La composition selon l'une quelconque des revendications 1 à 3, caractérisée en ce que le constituant b) est un copolymère greffé d'amidon.
  6. La composition selon l'une quelconque des revendications 1 à 5, caractérisée en ce que le constituant c) est choisi dans (i) le groupe comprenant polyéthylènes, polypropylènes, polyisobutylènes, polyamides, polyesters thermoplastiques, polyuréthanes thermoplastiques, polycarbonates, ou (ii) le groupe comprenant éthylène vinylacétate copolymères, éthylène/ vinylalcool copolymères, éthylène/ éthylacrylate copolymères, éthylène/ méthacrylate copolymères et leurs mélanges.
  7. La composition selon l'une quelconque des revendications 1 à 6, caractérisée en ce que le polymère du constituant c) absorbe de l'eau à un taux inférieur à 10% par 100 grammes de polymère à température ambiante.
  8. La composition selon l'une quelconque des revendications 1 à 6, caractérisée en ce que le polymère du constituant c) absorbe de l'eau à un taux inférieur à 5% par 100 grammes de polymère à température ambiante.
  9. La composition selon l'une quelconque des revendications 1 à 7, caractérisée en ce que la teneur en eau est de 5% à 30%, par rapport au poids du constituant amidon/eau.
  10. La composition selon l'une quelconque des revendications 1 à 9, caractérisée en ce que la teneur en eau est de 10% à 22%, par rapport au poids du constituant amidon/eau.
  11. La composition selon l'une quelconque des revendications 1 à 10 sous forme d'une masse fondue.
  12. La composition selon l'une quelconque des revendications 1 à 10 sous forme solide.
  13. La composition selon la revendication 12 sous forme de particules, de granules ou de pastilles.
  14. La composition selon la revendication 12 sous forme d'un article façonné choisi dans le groupe comprenant des récipients, des bouteilles, des tubes, des tiges, des emballages, des feuilles, des mousses, des films, des sacs, des sachets et des capsules pharmaceutiques.
  15. La composition selon la revendication 13 fondue à nouveau et traitée pour former un article façonné choisi dans le groupe comprenant des récipients, des bouteilles, des tubes, des tiges, des emballages, des feuilles, des mousses, des films, des sacs, des sachets et des capsules pharmaceutiques.

16. Les articles façonnés selon la revendication 14 et la revendication 15 caractérisés en ce que le procédé de façonnage comprend moussage, extrusion de films, moulage par compression, moulage par injection, moulage par soufflage, extrusion, coextrusion, formage sous vide, thermoformage et leurs combinaisons.

17. Un produit d'amidon thermoplastique déstructuré formé par le procédé comprenant:

1) fourniture d'un mélange comprenant:

- un amidon, essentiellement formé d'amylose et/ou d'amylopectine et ayant une teneur en eau entre 5% et 40% en poids;

- au moins un polymère, comme défini dans la revendication 1, en tant que constituant b);

- un polymère thermoplastique, comme défini dans la revendication 1, en tant que constituant c);

caractérisé en ce que la proportion de l'amidon déstructuré par rapport au constituant b) varie de 99:1 à 80:20 et caractérisé en ce que la somme des constituants b) et c) constitue au moins 50% et jusqu'à 80%, par rapport au poids total de la composition;

2) chauffage du dit mélange dans une vis et un fût d'un appareil de moulage par injection ou d'extrusion à une température comprise entre 130°C et 190°C et à une pression allant jusqu'à  $150 \times 10^5$  N/m<sup>2</sup> pour former une masse fondue et chauffage de la masse fondue pendant un temps assez long afin d'obtenir une déstructuration de l'amidon et une homogénéisation de la masse fondue;

3) façonnage de la masse fondue en un article; et

4) laisser l'article façonné refroidir en un article solide dimensionnellement stable.

18. Le produit selon la revendication 17 sous forme de particules, de granules ou de pastilles.

19. Le produit selon la revendication 17 sous forme d'un article façonné choisi dans le groupe comprenant des récipients, des bouteilles, des tubes, des tiges, des emballages, des feuilles, des mousses, des films, des sacs, des sachets et des capsules pharmaceutiques.

20. Le produit selon la revendication 17 fondu à nouveau et traité pour former un article façonné choisi dans le groupe comprenant des récipients, des bouteilles, des tubes, des tiges, des emballages, des feuilles, des mousses, des films, des sacs, des sachets et des capsules pharmaceutiques.